

Chemistry

Lecture 18

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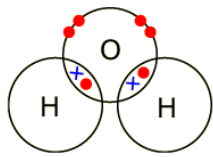
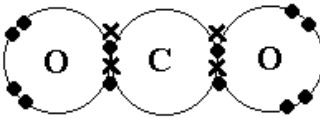
Chemical Bonding

Outline:

- ✚ Energetics of bond formation
- ✚ Atomic sizes
 - Atomic radii
 - Ionic radii
 - Covalent radii
- ✚ Ionization energy
- ✚ Electron affinity
- ✚ Electronegativity
- ✚ Types of bonds
 - Ionic (Electrovalent) bond
 - Covalent bonding
 - Co-ordinate (dative covalent) bonding
- ✚ Sigma and pi bond (VBT)
- ✚ Hybridization
 - sp^3 hybridization
 - sp^2 hybridization
 - sp hybridization
- ✚ The Valence Shell Electron Pair Repulsion theory
 - Postulates of VSEPR theory
 - Applications of VSEPR theory
- ✚ Bond energy
- ✚ Bond length
- ✚ Ionic character of covalent bond (Bond polarity)

Energetics of Bond formation

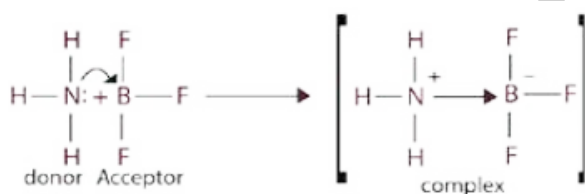
- Atoms form bonds which leads to decrease in energy
- Attractive forces and repulsive forces both operate when atoms approach
- Attractive forces tend to bring the two atoms close and P.E of system decreases
- Repulsive forces tend to push the atoms away and P.E of system is increases
- Bond distance/compromise distance/bond length:
 - ✓ Attractive forces dominate the repulsive forces
 - ✓ P.E of system is minimum
 - ✓ Stable molecule forms
- In case of H_2 , it is 75.4 pm and 436.5 kJmol^{-1} energy is evolved

Ionic (electrovalent) Bond		Covalent (electron pair) Bond	
Formed by complete transfer of electron from an atom with low I.E to an atom with high E.A		Formed by mutual sharing of electrons between two atoms	
Electron pair belongs to one bonded atom		Shared electron pair belongs to both bonded atoms	
Non-directional, non-rigid bond		Directional, rigid bond	
Shown by +ve and -ve charges		Shown by (— for single), (= for double), (≡ for tripe)	
Stronger than covalent		Weaker bond than ionic	
Compounds containing ionic bond are; → Ionic solids		Compounds containing covalent bond are; → Covalent and molecular solids (within molecule covalent)	
Bond is ionic if E.N difference > 1.7 with exception of HF (polar covalent)		Bond, non-polar (weaker) if E.N difference equal to 0.4 or less than 0.4 Bond, polar (stronger) if E.N difference > 0.4 but <1.7	
If E.N difference = 1.7 (50% ionic and 50% covalent)			
Best criteria (experimental) to check whether bond is covalent or ionic is to check conductivity in Molten state If substance conducts (ionic bond present), if does not conduct (covalent bond present)			
Atom with low I.E forms cation Best conditions for its formation; (i) Smaller charge of formed cation (ii) Large size of atom	Atom with high E.A forms anion Best conditions for its formation; (i) Smaller charge of formed anion (ii) Small size of atom	Hydrogen: $\text{H} \times \text{H}$ or $\text{H} - \text{H}$ Chlorine: $\text{Cl} \times \text{Cl} \times$ or $\text{Cl} - \text{Cl}$	
Usually IA, IIA elements form ionic bond with VIA, VIIA elements with few exceptions, Al (IIIA) forms ionic bond with "F, O" i.e. AlF ₃		HF: $\text{H} \times \ddot{\text{F}}:$ or $\text{H}-\text{F}$ Oxygen: $\text{O} \times \text{O} \times$ or $\text{O}=\text{O}$	
NaCl: $_{11}\text{Na} (1s^2, 2s^2, 2p^6, 3s^1) \xrightarrow{\text{Oxidation}} \text{Na}^+ (1s^2, 2s^2, 2p^6) + 1e^- \quad \Delta H = 496 \text{ kJmol}^{-1}$ $_{17}\text{Cl} (1s^2, 2s^2, 2p^6, 3s^2, 3p^5) + 1e^- \xrightarrow{\text{Reduction}} \text{Cl}^- (1s^2, 2s^2, 2p^6, 3s^2, 3p^6) \quad \Delta H = -349 \text{ kJmol}^{-1}$ $\text{Na}^+ + \text{Cl}^- \rightarrow \text{NaCl} \quad \Delta H = -787 \text{ kJmol}^{-1}$		Water: 	
CaO: $_{20}\text{Ca} (1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2) \xrightarrow{\text{Oxidation}} \text{Ca}^{2+} (1s^2, 2s^2, 2p^6, 3s^2, 3p^6) + 2e^-$ $_{8}\text{O} (1s^2, 2s^2, 2p^4) + 2e^- \xrightarrow{\text{Reduction}} \text{O}^{2-} (1s^2, 2s^2, 2p^6)$ $\text{Ca}^{2+} + \text{O}^{2-} \rightarrow \text{CaO}$		Carbon dioxide: 	
No bond is 100% ionic because when cation and anion approach each other			
(i) Repulsion b/w their electronic cloud increases			
(ii) Polarizability increases			

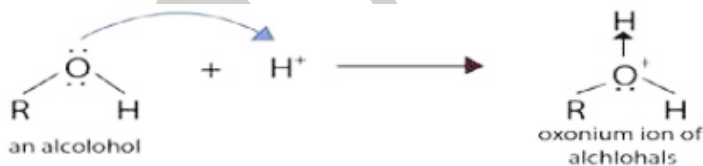
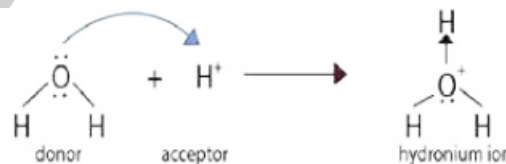
(iii) Covalent character increases	
CsF has maximum ionic character i.e. 92%, NaCl = 72%	
Strength of ionic bond \propto Lattice energy	Strength of covalent bond \propto Bond energy

Co-ordinate (dative covalent) Bond:

- Bond formed when shared pair is donated by one of the bonded atom
- Donor **i.** Atom that donates **ii.** Lewis base **iii.** Possess lone pair
- Acceptor **i.** Atom that accepts **ii.** Lewis acid **iii.** Deficient in electron in its octet
- Distinction b/w covalent and coordinate covalent disappears after formation
- $\text{NH}_3(\text{g})$ (donor N) forms coordinate covalent bond with $\text{BF}_3(\text{g})$ (acceptor B) to form neutral complex



- Water donates its electron pair to H^+ ion to give H_3O^+ ion. All the three bonds between oxygen and hydrogen have equal status
- Every bond is 33% coordinate covalent and 66% covalent
- Similarly, all the alcohols and ethers offer their lone pairs to H^+ , just like H_2O to give coordinate covalent bonds.
- The ions so produced are called oxonium ions



VSEPR Theory

By Nyholm and Gillespie

Postulates:

1. Electron pairs [lone pair (ℓp) and bond pair (bp)] determine geometry
2. Electron pairs (ep) remain at maximum distance to avoid repulsion
3. ℓp (attracted by one nuclei) occupies more space than bp (attracted by two nuclei)
 $\ell p - \ell p > \ell p - bp > bp - bp$ (repulsion order)
4. Double/triple (occupy more charge density than single) behave like single bond while determining the shapes

- For **regular geometry**; No lone pair on central atom, polyatomic molecule consists of only two type of atoms
- For **irregular geometry**; At least one lone pair OR at least one dissimilar atom attached to central atom (both scenarios will also give irregular)

Type	Sub-type	b.p	ℓ.p	e.p	Hybridization	Geometry	Angle	Examples
AX ₂	AB ₂	2	0	2	Sp	Linear	180°	BeCl ₂ , MgCl ₂ , CO ₂ , HCN
AX ₃	AB ₃	3	0	3	sp ²	Trigonal planner	120°	BCl ₃ , BF ₃ , SO ₃ , BH ₃
	AB ₂ L	2	1	3	sp ²	Bent (angular or V-shaped) Or Distorted triangular	<120°	PbCl ₂ , SnCl ₂ , SO ₂
AX ₄	AB ₄	4	0	4	sp ³	Tetrahedral	109.5°	CH ₄ , NH ₄ ⁺ , SiCl ₄ , CCl ₄
	AB ₃ L	3	1	4	sp ³	Trigonal pyramidal	<109.5°	PH ₃ , NH ₃ (107.5°), NF ₃ (102°)
	AB ₂ L ₂	2	2	4	sp ³	Bent (angular or V-shaped)	<109.5°	H ₂ S (92°), H ₂ O (104.5°)
AX ₅	AB ₅	5	0	5	sp ³ d/dsp ³	Trigonal bipyramidal	90°, 120° two each	PCl ₅
AX ₆	AB ₆	6	0	6	sp ³ d ² /d ² sp ³	Octahedral	90°	SF ₆

Limitations of VSEPR:

- Only explains shapes, no reason for bonding
- Not applicable to single electron system
- Not applicable to transition elements

Valence Bond Theory

- ◆ Explain bond formation
- ◆ Atomic orbitals must overlap for bond formation
- ◆ Atomic orbitals overlapping must be half filled
- ◆ Atomic orbitals $\xrightarrow{\text{Overlap}}$ Molecular orbitals
- ◆ Atomic orbitals $\xrightarrow{\text{Intermix}}$ Hybrid orbitals (all hybrid orbitals form σ -bond or lone pair)
- ◆ Larger the overlap stronger is the bond

Sigma Bond (σ)	Pi Bond (π)
Formed by head on/horizontal (axial) overlap	Formed by sideways/vertical (lateral) overlap
Charge density around the axis joining two nuclei	Charge density above and below the axis joining two nuclei
Charge density is symmetrical	Charge density is unsymmetrical
Larger overlap than pi, so stronger than pi	Lesser overlap than sigma, so weaker than sigma
Sigma bond has bond rotation	Pi bond has no bond rotation
Result of s-s, s-p, p-p overlap and strength is;	Result of only p-p overlap after sigma bond is

p-p > s-p > s-s	formed 1 st
If more than 1 half filled p-orbitals are available, they prefer sigma bond 1 st and then rest will form pi	
Multiple bonds have only one sigma bond	

Limitations of VBT:

Does not explain;

- ☒ Formation of coordinate covalent bond
- ☒ Paramagnetic behavior
- ☒ Odd electrons in molecule or ion
- ☒ Four bonds of Carbon

Hybridization

- ☞ Atomic orbitals of slightly different energy and shape intermix to give equal number of degenerate hybrid orbitals (same shape) which have different shapes from parent atomic orbitals
- ☞ Hybrid orbitals have one lobe larger in size than the other
- ☞ Hybrid orbitals cannot form pi bond
- ☞ Half filled and completely filled atomic orbitals can intermix to form hybrid orbitals
- ☞ Energies of hybrid orbitals are lower from parent atomic orbitals
- ☞ sp^3 , sp^2 and sp

sp^3 Hybridization:

- One s-orbital intermixes with three p-orbitals to form four sp^3 hybrid orbitals
- sp^3 hybrid orbital has 25% s-character and 75% p-character
- All hybrid orbitals are at 109.5° from each other
- Tetrahedron geometry is related with it
- Angle for regular geometry = 109.5°
- Examples:
 - ✓ Methane (CH_4 = 4 σ -bonds through overlap of sp^3 -hybrid orbitals of carbon with s-orbital of hydrogen)
 - ✓ Ethane (C_2H_6 = 7 σ -bonds) 1 σ -bond is through overlap of sp^3 -hybrid orbital one carbon with sp^3 -hybrid orbital other carbon while 6 σ -bond is through overlap of sp^3 -hybrid orbitals of carbon with s-orbital of hydrogen
 - ✓ Ammonia [3 σ -bonds through overlap of sp^3 -hybrid orbitals of nitrogen with s-orbital of hydrogen] (one lone pair, 107.5°)
 - ✓ Water [2 σ -bonds through overlap of sp^3 -hybrid orbitals of oxygen with s-orbital of hydrogen] (two lone pairs, 104.5°) etc

sp² Hybridization:

- One s-orbital intermixes with two p-orbitals to form three sp² hybrid orbitals
- sp² hybrid orbital has 33.3% s-character and 66.7% p-character
- All hybrid orbitals are at 120° from each other
- Triangular planar geometry is related with it
- Angle for regular geometry = 120°
- Examples:
 - ✓ Ethene (C₂H₄ = 5 σ-bonds + 1 π-bond) 1 σ-bond is through overlap of sp²-hybrid orbital one carbon with sp²-hybrid orbital other carbon while 4 σ-bond is through overlap of sp²-hybrid orbitals of carbon with s-orbital of hydrogen. Pi bond is formed by sideways overlap of unhybridized atomic orbitals of both carbons i.e. 2p_z-2p_z
 - ✓ BF₃ (3 σ-bonds through overlap of sp²-hybrid orbitals of boron with p-orbital of fluorine)

sp Hybridization:

- One s-orbital intermixes with one p-orbitals to form two sp hybrid orbitals
- sp hybrid orbital has 50% s-character and 50% p-character
- All hybrid orbitals are at 180° from each other
- Linear geometry is related with it
- Angle for regular geometry = 180°
- Examples:
 - ✓ Ethyne (C₂H₂ = 3 σ-bonds + 2 π-bond) 1 σ-bond is through overlap of sp-hybrid orbital one carbon with sp-hybrid orbital other carbon while 2 σ-bond is through overlap of sp-hybrid orbitals of carbon with s-orbital of hydrogen. Pi bonds are formed by sideways overlap of unhybridized of atomic orbitals both carbons i.e. 2p_y-2p_y, 2p_z-2p_z
 - ✓ BeCl₂ (2 σ-bonds through overlap of sp-hybrid orbitals of beryllium with p-orbital of chlorine)

Bond Energy

☞ Average amount of energy required to break all bonds of particular type in mole of a substance

☞ Also called bond enthalpy

☞ Unit is kJmol⁻¹

☞ **Factors:**

- Bond Energy ∝ (i) Bond order (ii) Polarity (E.N difference) (iii) s-character (sp > sp² > sp³)
- Bond Energy ∝ (i) $\frac{1}{\text{Size}}$ (ii) $\frac{1}{\text{Lone Pairs}}$
- **Bond Energy ∝ $\frac{1}{\text{Bond Length}}$**

For comparison, see table given in the TEXT BOOK

Applications

- ☞ Enthalpy change of a reaction (Main/important)
- ⚙ Gives comparison of bond strengths
- ⚙ Helps in structures and bonding
- ⚙ Explains mechanism of chemical reaction

Bond Length

- 📖 Distance between nuclei of two covalently bonded atoms
- 📖 Bond Length \propto Size
- 📖 **Bond Energy $\propto \frac{1}{\text{Bond Length}}$** (so all the factors of B.E will have opposite effect on B.L)
- 📖 Determined by electron diffraction, X-rays diffraction or spectral studies
 - ✓ Usually experimental bond length is equal to sum of covalent radii of both atoms i.e. C-Cl has bond length 176 pm which is equal to sum of covalent radii of C and Cl (77 + 99 = 176 pm)
 - ✓ In case of more polarity this is not true i.e. Si-F has experimental bond length 154-159 pm, while sum of covalent radii of Si and F is (117 + 64 = 181 pm)
 - ✓ More the polarity (E.N difference), greater will be the difference between experimental and calculated values

For comparison, see table in TEXT BOOK

Bond Polarity

- 📖 Bond polarity \propto E.N difference (for diatomic molecules)
- 📖 Experimental criteria for polarity is dipole moment (for all diatomic as well as polyatomic molecules)
- 📖 Non-polar ($\mu = 0$), Polar ($\mu \neq 0$) and greater " μ ", more will be polarity
- 📖 **Dipole Moment (μ):**
 - Product of the electric charge (q) and the distance between the positive and negative centers (r)
 - It's a vector quantity with two units [mC (SI), Debye (Non-SI)]
 - Direction from positive to negative end
- 📖 Dipole moment provides two types of information about the molecular structure;
 - **Percentage ionic character of a bond** $= \frac{\mu_{obs}}{\mu_{ionic}} \times 100$
 - **Prediction of Isomers** [trans has $\mu = 0$, cis has $\mu \neq 0$]
 - **Angles between the bonds or the geometry of molecules**
- 📖 **Bond Angles or the Geometry of Molecules:**
 - Water: [$\mu = 1.85$ D], (Angle = 104.5°), (Structure is angular or bent)]
 - SO₂: [$\mu = 1.61$ D], (Structure is angular or bent)]
 - H₂S: [$\mu = 0.95$ D], (Structure is angular or bent)]

- CO: ($\mu = 0.12$ D)
- CO₂/CS₂: [$\mu = \text{zero}$], (Structure is Linear)]
- Molecules with regular geometries (BF₃, CH₄) have zero dipole moment
- Molecules with irregular geometries (NH₃, H₂O) have dipole moment

For comparison, see table in TEXT BOOK

Type of Bonding in Substances

Substances	Forces/Bonds
HCl + Ar	Debye Forces
Propanone + Trichloromethane HF, H ₂ O, NH ₃	H-bonding Forces (b/w molecules) Covalent bond (within molecule)
HCl, HBr, Aldehyde, ketones	Dipole-dipole Forces (b/w molecules) Covalent bond (within molecule)
Noble gases, Hydrocarbons, Halogens	London Forces (b/w molecules) Covalent bond (within molecule)
Ice	Covalent bonding (within molecules) H-bonding (b/w molecules)
NH ₄ Cl	Covalent + Coordinate + Ionic
KOH	Ionic bond + Covalent
NaCN	Ionic + Covalent

Best of Luck